Fumarolic alteration products at Sousaki (Greece): occurrence and environmental impact

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Abstract

Fumarolic alteration crusts and efflorescences have been sampled at the Sousaki solfataric field. Samples have been analysed for mineralogical (XRD) and chemical composition (HNO_3 digestion and leaching with distilled water). Results show that mineralogical and chemical compositions (major, minor and trace metals) are controlled by microenvironmental conditions. The sample collected in the anoxic part of a cave is composed almost exclusively by native sulfur. The samples collected in the oxidizing part of the cave and outside in relatively sheltered position are mainly composed by very soluble sulfates. Chemical composition evidence strong enrichments in Al, Ca, Cr, Fe, Mg and Ni which are present in highly soluble form and derive from the fumarolic alteration of the outcropping rocks (Marls and peridotites). One sample collected outside the cave, well exposed to atmospheric agents, is composed almost exclusively of gypsum and the chemical composition reveals, with respect to the previous samples, a relative enrichment of elements (Ba, Ca, K, Pb and Sr) forming less soluble sulfates.

The presence of toxic metals like Al, Cr and Ni in high concentrations and highly soluble form evidences the potential impact of the fumarolic activity on the local environment.

Keywords: Hydrothermal alteration products; sulfates; toxic metals; elements' mobility.

1. INTRODUCTION

Mobility of elements in the exogenic cycle depends on chemico-physical parameters during weathering processes. While some of the elements displaying a high affinity for the aqueous phase are easily mobilized by water, other elements on the contrary, are retained in the soils that are growing as a consequence of weathering processes [1]. These elements can be either retained in primary mineral phases, which are stable or metastable at the earth's surface or incorporated in newly formed secondary minerals. The mobility of some elements in the soils can be also severely limited by specific or non-specific adsorption onto organic matter, Al- and Fe-amorphous phases, phyllosilicates and iron-hydroxydes.

Elements' mobility can be extremely favored by a strongly acidic environment. Such conditions can be the result of natural processes like for example magmatic/geothermal degassing or oxidation of sulfide minerals. The consequent elements' mobilization has often a severe impact on the surrounding environment [2]. For instance, the Kawah Ijen Crater Lake in East Java (Indonesia) has a pH < 0.3, and is the feeding source of the extremely acidic and metal-polluted river Banyupahit (Indonesian name for "bitter river"). The lake has a significant impact on the river ecosystem as well as on a densely populated area downstream [3,4], where agricultural fields are irrigated with low pH waters (2.5 - 3.5) and whose metal concentrations exceed international quality guidelines, reaching extremely high values especially for Fe (up to 1600 mg/L) and Al (up to 3000 mg/L).

Another important example can be found in the Iberian Pyrite Belt (SW Spain), which hosts one of the largest concentrations of massive sulfide deposits in the world, with at least 4500 years of mining history. The most part of this mining district corresponds to the drainage basin of the Tinto and Odiel rivers. These, amongst the rivers affected by acid mine drainage worldwide, represent an extreme case of pollution with low pH values (between 1.0 and 3.0) and very high metal and metalloid concentrations [5]. The metal discharges in the Huelva estuary (in which both rivers merge) have a regional impact, and increase significantly, at least seasonally, metal inputs to the Mediterranean Sea [6].
Environmental studies of the processes generating metal-rich acid waters have highlighted the importance of metal-sulfate minerals forming upon evaporation, oxidation and neutralization processes [7]. Metal-sulfate salts are common around active crater lakes, fumaroles and acid hot springs. In these environments, H_2S oxidizes to elemental sulfur, which accumulates and is further oxidized to form sulfuric acid. The acid reacts with the surrounding bedrock leading to the formation of a variety of metal-sulfate minerals. Some of these minerals are highly soluble and store metals and acidity only temporarily, whereas others are insoluble and improve water quality by removing metals from solutions.
The study area of this paper, Sousaki, is a presently inactive volcanic area hosting a geothermal reservoir. Geothermal activity, still recognizable by a series of low temperature gas manifestation, is responsible of the widespread alteration of the outcropping rocks in the area. The main manifestations are hosted within caves whose walls are covered by alteration products in the form of crusts and efflorescences [8]. The caves provide a sheltered, more or less stable environment in which the alteration process can take place and where its products can persist. However the same products can be found during dry periods also at minor manifestations although in open skies position. This study presents the results of mineralogical and chemical analyses of the alteration products collected in the area. Leaching experiments were also performed to get insights on the mobility of the elements incorporated in the alteration products, and the possible environmental impacts are discussed.

2. MATERIALS AND METHODS

2.1 Geologic description of the area

The Sousaki area is located about 65 km west from Athens, near the Isthmus of Corinth. It represents one of the volcanic systems of the active Aegean volcanic arc [9,10]. Its activity spanned from mid- to late-Pliocene (age determinations range from 4.0 to 2.3 Ma). The sparse volcanic outcrops, with an estimated total volume of less than 1 km^3, consist in lava flows and domes and subordinated tuffs of dacitic to rhyolithic composition [10,11].
Both the vent distribution and the shape of the edifices are controlled by the E-W and the NW-SE extensional tectonic lineaments of the area, which were present since Pliocene and continue to be active up to the present [10].
Besides volcanic rocks the following formations crop out in the area [12]:
1. Quaternary sediments: consisting of unconsolidated material with sand and rounded and angular pebbles in the torrent beds, loose sandy – clayey material and alluvial sediments.
2. Neogene sediments: composed of marly conglomerates and marly sandstones
3. Post-upper Cretaceous ophiolithic nappe: consisting of slightly serpentinized peridotites, serpentinites and bodies of basic composition.
4. Upper Triassic–lower Cretaceous limestones.
The climate is of a dry Mediterranean type with an average rainfall of about 400 mm. The rainfall distribution displays great inter- and intra-annual variations, with 80% of the annual rainfall occurring between October and March, while rainfall is almost non-existent during the dry season from June to September.

2.2 Geothermal manifestations

Drilling exploration campaigns, performed during the late seventies, assessed the presence of a low enthalpy geothermal field, revealing two permeable formations at shallow depth (< 200 m) and one at deeper levels (500 – 1100 m). All geothermal waters are of Na-Cl type and display temperatures in the range 50 – 80 °C and salinities in the range 39 – 49 g/l [13]. Widespread fumarolic alteration and warm (35 – 45 °C) gas emissions are still recognizable [14]. The geothermal reservoir and its degassing are likely controlled by active tectonic structures. Extended argillification-silicification of the rocks characterizes an area of about 200 × 700 m with widespread surface emanations called Theochoma. The main vents are found at the bottom of two caves on the flank of a hill. The caves called "big" and "small" have the following dimensions (height × width × depth) 8×3×10 m and 4×1.5×4 m respectively. The emanating gases, being denser than atmospheric air, flow on the floors of the caves and eventually spill out from their mouth dispersing in the atmosphere after descending the flanks of the hill. This phenomenon can be seen when the atmospheric temperature is very low and the water vapor contained in the geothermal gases condenses creating a thin fog layer at the contact between the cold atmospheric air and the warm geothermal gases.

The gas flux being almost constant with time creates a clear separation in the caves' atmosphere with an anoxic part on the floor, evidenced on the walls by a clear-cut line separating the lower fumarolic alteration products, mainly composed of native sulfur and sulfides, from the upper more oxidizing portion composed mainly of sulfates [8,14].

The chemical composition of the gases point to a typical geothermal composition with CO_2 as the main component (>95%) and CH_4 (~8000 ppm) and H_2S (~1200 ppm) as minor components [14]. It has been estimated that the two main gas manifestations of Sousaki release about 2 Mg of CO_2 and 2 kg of H_2S each day [14].

2.3 Sample collection and analysis

Nine samples of alteration products have been collected in three different places of the fumarolic field. Six of the samples were taken from the walls of the small cave. One of these (GR1) represents the wall's coating of the portion of the cave permanently saturated with the geothermal gases, while the remaining five (GR2 – GR6) were collected above the saturation surface at different heights. One sample (AL1) was collected on the ground outside the caves at a distance of about 10 m from the entrance, well exposed to atmospheric agents. Two samples (AG1 and AG2) were collected at a minor gas manifestation seeping from the ground at the base of a small cliff in partially sheltered position.

Samples were gently scraped from the walls with the PP containers in which they were stored. In the laboratory they were split in two aliquots for mineralogical and chemical analysis.

Mineralogical analysis was carried out by X-ray diffractometry (XRD), using a CuKα radiation Ni filtered, scanning rate 2° 2θ min^{-1} in the range 2–60°.

The sample for chemical analysis was firstly ground in an agate mortar and then further split in two aliquots. The first one was mineralized according to the following procedure. About 70 to 200 mg of the sample dried at 40 °C overnight was dissolved in a Teflon vessel with 6 ml HNO_3 (Merck Suprapur) and 4 ml milliQ water using a microwave oven. After cooling down the solution was filtered (0.45 μm) and diluted with milliQ water to 50 mL. A second oven-dried sample aliquot was leached with milliQ water with a sample/water ratio of about 0.01 for 4 hours with constant stirring. The solution was subsequently filtered through 0.45 μm filter. Both types of solution were analyzed for Al, As, B, Ba, Cd, Co, Cr, Cs, Cu, Fe, Hg, Li, Mn, Mo, Ni, Pb, Rb, Sb, Se, Sr, Th, U, V and Zn by ICP-MS (Agilent 7500 CE) and Ca, K, Mg and Na by IC (Dionex DX120). The analytical accuracy was checked analyzing reference materials (SLRS-4 of the National Research Council of Canada and Spectrapure Standards SW1). Repeatability was always better then ± 10% for ICP-MS and ± 5% for IC.

3. RESULTS AND DISCUSSION

3.1 Mineralogical composition

The results of the X-ray diffraction analyses are displayed in Table 1. Basing on their mineralogical composition, the samples can be subdivided in three groups. Sample GR1, collected in the anoxic part of the cave, belongs to the first group and is composed almost exclusively of Native Sulfur. The second group comprises all the samples collected in the oxidized part of the cave and the two samples collected outside the cave in relatively sheltered position. These samples are composed mainly of sulfates. Calcium sulfate, both as Anhydrite or Gypsum, is ubiquitous. Other detected sulfates (Kieserite, Epsomite, Hexahydrite, Wairakite, Magnesiocopiapite, Alunogen) are typical of hydrothermal environment. Phases with different hydratation state are found depending on local environmental conditions. Notably phases with lower hydratation state like Kieserite ($MgSO_4 \bullet H_2O$) and Anhydrite ($CaSO_4$) are found at the top of the cave where both absolute and relative humidity are lower with respect to the lower part of the cave. Also the samples collected outside the caves are probably exposed to environmental conditions leading to higher hydratation states. Higher humidity conditions favor the formation of Hexahydrite ($MgSO_4 \bullet 6H_2O$) or Epsomite ($MgSO_4 \bullet 7H_2O$) and Gypsum ($CaSO_4 \bullet 2H_2O$).
Sample AL1, which belongs to the last group, is almost exclusively composed of gypsum.

Table 1. Results of the XRD analysis.

Sample	Mineral phases
GR1	**Native Sulfur**
GR2	Kieserite, Anhydrite
GR3	Anhydrite, Cristobalite, Alunogen
GR4	Anhydrite, Hexahydrite, Wairakite
GR5	Magnesiocopiapite
AG1	Epsomite, Gypsum
AG2	Hexahydrite, Gypsum, Magnesiocopiapite
AL1	**Gypsum**

3.2 Chemical composition

The results of the chemical analyses are summarized in Table 2. Values obtained from HNO_3 mineralization can be considered as near total concentrations because generally no visible residue was present after treatment. The only exceptions were sample GR1 and AL1 where yellow translucent and dark opaque residues were respectively observed. Some of the analyzed elements (Cd, Hg, Sb, Se and Th) were always at or below detection limit and were excluded from the table. Other elements (B, Ba, Cs, Cu, Li, Mo, Pb, Rb, U and V), with limited exceptions, display concentrations always below some tens of µg/g. Al, Ca, Fe and Mg display the highest variability, ranging from hundreds up to more than 100000 µg/g. Cr and Ni show also elevated concentration (thousands of µg/g). Samples obtained from leaching experiments display concentrations which are the same as (within analytical error) or lower than those obtained with HNO_3 mineralization, indicating solubilities in water that vary from nearly 100% down to 1% for the different elements in the different samples.
Basing on chemical composition, the samples can be subdivided in the same three groups obtained from mineralogical analysis. Sample GR1 (anoxic part of the cave) displays very low concentrations for all elements. Only few elements (Ca, Fe, K, Mg and Na) display values higher than 100 µg/g. It is improbable that most of the elements' contents remained in the insoluble residue probably composed entirely of sulfur. The low concentrations are best explained by the fact that the

lattice of native sulfur does not allow for extended substitutions and that the elements found derive mainly from debris falling from the upper walls of the cave.
The presence of highly soluble sulfates in the samples of the second group justifies the high concentrations of Al, Fe and Mg. The relatively high concentration of Ca derives from the ubiquitous presence of either anhydrite or gypsum. The presence of Nickel-hexahydrite, which was not identified in the present study but was previously found at Sousaki [8], explains the relatively high concentrations of Ni.
Most of the analyzed elements are found in the samples of this group in soluble form further evidencing their affinity to highly soluble mineral phases. In particular all the elements contained in high concentrations (Al, Ca. Fe and Mg) and many others (Co, Cr, Cs, Cu, Li, Mn, Ni, Rb, Sr, U and Zn) display average solubilities ranging from 70 to 94%. On the contrary, As, B, Ba, K, Mo, Na, Pb and V display lower solubilities (4 – 56%). Except for As (up to 720 μg/g) and K (up to 50000 μg/g) the low solubility elements display total concentrations rarely exceeding 10 μg/g.

Table 2. Results of the chemical analysis (values in μg/g)

	Al	As	B	Ba	Ca	Co	Cr	Cs	Cu	Fe	K	Li	Mg	Mn	Mo	Na	Ni	Pb	Rb	Sr	U	V	Zn
Sample	Mineralised with HNO_3																						
GR1	60	3.58	9.79	1.02	4120	1.39	7.19	< 0.1	1.16	177	12000	0.12	1310	5.20	0.20	283	30.8	1.44	< 0.1	1.80	< 0.1	0.11	21.8
GR2	2660	127	7.10	1.61	16500	175	338	10.6	13.9	17800	18100	9.22	142000	466	1.63	2160	3600	0.84	17.6	62.5	0.87	4.09	41.2
GR3	3950	26.7	14.0	2.88	32500	184	174	1.81	11.5	3440	29700	7.01	116000	673	< 0.3	864	3570	0.66	1.69	65.9	1.91	2.25	32.4
GR4	43000	16.0	4.76	2.06	21200	431	2140	1.20	27.9	10200	26500	2.19	52900	1065	0.19	632	6940	0.27	0.81	27.5	1.43	2.55	61.9
GR5	23300	720	3.16	< 0.1	4230	249	3900	3.94	17.6	105000	22800	8.30	46200	992	1.13	534	7660	< 0.1	3.05	4.86	1.56	20.9	44.4
GR6	54600	57.8	8.79	0.39	2120	655	7370	4.14	241	8700	33700	12.0	54300	3670	0.41	1060	8790	0.55	3.14	14.7	17.0	3.58	117
AG1	244	8.12	1.95	1.80	20100	60.4	37.4	0.67	2.28	1220	22700	3.03	147000	154	0.16	571	2170	0.35	0.43	80.2	0.11	0.83	6.35
AG2	5610	230	2.28	0.49	479	141	1510	1.94	5.90	101000	10200	0.95	1180	519	0.73	145	2850	0.13	1.77	34.9	0.29	18.6	25.9
AL1	641	10.5	2.97	117	175000	1.36	122	2.01	0.62	901	50000	0.53	895	4.92	0.43	723	19.0	15.3	2.85	198	0.03	2.72	4.64
	Leached with distilled water																						
GR1	52	1.10	0.68	0.08	663	1.33	6.08	0.11	0.06	155	6320	0.09	121	4.73	< 0.1	169	30.6	0.34	0.16	1.82	< 0.1	0.06	4.71
GR2	3930	86.6	0.97	1.09	2630	149	281	11.4	12.1	16500	3140	9.86	26700	421	1.17	439	3340	0.67	18.6	59.8	0.85	3.99	35.9
GR3	5570	1.47	0.71	0.63	34200	164	137	1.60	9.16	2160	12300	7.42	113000	625	< 0.1	579	3420	0.29	1.56	67.8	1.79	0.20	18.3
GR4	41600	10.7	0.24	0.59	13900	333	1630	0.87	18.5	8250	10900	1.70	35300	800	< 0.1	237	5480	0.12	0.67	23.5	1.03	1.80	42.6
GR5	24300	53.3	< 0.1	< 0.1	2640	197	2950	3.53	13.1	61800	10800	7.87	34600	753	< 0.1	403	6220	0.02	2.75	4.67	1.24	4.04	34.4
GR6	47700	21.6	< 0.1	0.10	2900	447	5140	3.25	179	7080	9890	10.1	44800	2530	0.15	669	6220	0.40	2.58	12.4	12.8	2.04	81.0
AG1	195	1.23	< 0.1	0.53	12300	52.9	20.6	0.50	1.87	872	6470	2.82	113000	137	< 0.1	236	2020	0.21	0.35	65.2	0.09	0.08	5.35
AG2	5370	99.6	< 0.1	0.22	8050	119	1170	1.63	5.14	78700	6100	0.92	40600	386	0.51	114	2360	0.04	1.60	36.6	0.25	16.9	21.6
AL1	34	0.40	1.72	1.33	42000	0.38	4.74	0.17	0.60	28.4	10800	0.14	422	1.08	0.16	320	5.34	3.18	0.24	98.8	0.01	0.03	1.46

In the last group (sample AL1) most elements show generally lower concentrations with respect to the samples of the previous group. They also display a lower solubility (1 – 58%). Only few elements display concentrations that are up to two orders of magnitude higher than those of the previous group. Notably these elements (Ba, Ca, K, Pb and Sr) form sulfate phases with low or very low solubility. In this sample, which was exposed to atmospheric agents, low solubility phases were enriched due to the leaching of the most soluble phases.

3.3 Environmental impact

When acid drainage waters are produced by oxidation of sulfide ore mining residues, many toxic elements may be mobilized and transported offsite at concentrations that can be of environmental concern [7,15]. Similarly also the dissolution of the alteration products of fumarolic and solfataric fields may have a strong environmental impact [16].
At Sousaki, efflorescences and crust within the cave are effectively sheltered from atmospheric agents and will be dissolved only rarely when intense rainfall produce infiltrations from the roof. But soluble alteration products form also outside the caves, especially within zones with high hydrothermal gas fluxes from the soil. Such zones cover an area of several thousands of m^2 [14] and are drained by a seasonal creek. The strong seasonality of rainfall in the area probably produces a large peak in its water concentration for many harmful elements when intense autumn precipitations dissolve the sulfates that formed during the long summer dry spell. Such flux of harmful elements could impact biota along the course of the creek and on the marine environment close to its mound about 1 km downstream. Although such impact has not been yet studied it is worth noting that

vegetation along the creek downstream of the hydrothermal manifestations is very stunted probably due to the bioavailability of the mobilized toxic elements.

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